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Abstract:

Understanding the gas-phase and gas-surface collision dynamics of highly vibrationally excited NO is necessary to model the rovibrational population distribution and infrared signatures of this important molecules in the upper atmosphere. Energy and momentum exchange between gas phase molecules and surfaces (especially oxidized surfaces) is also an important factor in the calculation of satellite drag coefficients. In this research the stimulated emission pumping method is used in combination with conventional molecular beams techniques to control the vibrational excitation, quantum state identity and collision energy of reactants in gas phase and gas-surface reactions. Results allow a better understanding of the collision dynamics controlling the state-specific population of vibrationally excited NO in the upper atmosphere and around satellites in low earth orbit.

Project Title: Gas-phase and surface reactivity of highly vibrationally and translationally excited molecules

Principal

Investigator: Alec M. Wodtke, Department of Chemistry, University of California Santa Barbara, Santa Barbara CA 93106, Grant #F49620-95-1-0234

Objectives:

Highly vibrationally excited molecules have been observed to play an important role in determining the infrared emission spectrum of the upper atmosphere. The objective of this research is to understand, predict, and control the reactivity and the flow of energy in highly vibrationally excited molecules. To this end, information is needed on collisional energy transfer and reactivity of highly vibrationally excited molecules with other molecules and with surfaces. This knowledge may then be used in atmospheric chemistry models to improve our detection and control of infrared signatures. Topics of interest include: the effect of vibrational excitation on reaction probability, chemical branching and rate of infrared emission, and survival of vibrational excitation upon collisions with surfaces.

Quantum state selective laser-based optical pumping schemes such as *stimulated emission pumping* (SEP) are used to prepare highly vibrationally excited molecules. Crossed molecular beams methods are used to study the rotational and vibrational energy exchange as well as chemical reactivity of these species under single collision conditions. Ultra-high vacuum surface science methods are combined with the afore-mentioned optical pumping and molecular beams methods to study gas-surface interactions.

Results of the project:

We have designed and built two new experimental stations for the study of the collision dynamics of highly vibrationally excited molecules. The first is a crossed molecular beams apparatus. In this machine we prepare highly vibrationally excited molecules using stimulated emission pumping (1-3) (SEP). These molecules cross a second molecular beam and state-specific detection of gas-phase collision processes is then carried out. The second apparatus is a hybrid molecular-beam/UHV-surface-science machine. In this experiment, highly vibrationally excited molecules are again prepared with SEP in a molecular beam. These molecules then interact with a well characterized surface in the UHV chamber and lasers or mass spectrometry are used to probe the gas-surface collision dynamics.

A schematic of the "gas-phase machine" is shown in Fig. 1. This apparatus has been applied to a

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number of experimental problems concerning the collision dynamics of highly vibrationally excited molecules. For example, we have examined rotational inelastic scattering of NO by He, where NO is prepared in single parity-selected quantum states of $v=20$ of the ground electronic state. A comparison to *ab initio* predictions of the inelastic scattering cross-sections was thereby possible (calculations carried out by Millard Alexander). The theoretical approach was approximate. A 2D *ab initio* potential surface was calculated for He/NO with the NO bond length frozen at the vibration-averaged bond length of NO($v=20$), $\langle r \rangle_{20}$. Even with such an apparently drastic assumption, agreement between the experimental results and the scattering calculations on the PES is excellent, confirming, the validity of both the experimental and theoretical approaches.

In another experiment in the "gas-phase machine", inelastic near-resonant V-V scattering was observed under single collision conditions. Experiments showed the state-to-state dynamics of near resonant V-V energy transfer of NO($v \rightarrow v-1$) + N₂O(000 \rightarrow 001) for $v=22-20$. It was found that the energy defect of the near resonant V-V energy transfer is largely accommodated by the NO rotational degrees of freedom. Attempts to understand this from a theoretical point of view are ongoing.

A new approach to the determination of infrared radiative lifetimes was also developed with this machine. In this experiment, the second molecular beam in Fig. 1 is turned off. The highly vibrationally excited molecules prepared by SEP at the "Preparation Zone" of the machine are allowed to fly under collision free conditions to the "Detection Zone". The radiative relaxation during this ($\sim 80\mu\text{s}$) flight-time populated lower vibrational levels through the usual infrared selection rules. $\Delta v = -1, -2, -3$, and -4 transitions were observed. By comparing to aspects of the UV radiative relaxation, precise IR radiative lifetimes could be derived for individual vibrational states of highly vibrationally excited NO. This is the only example where the IR radiative lifetimes of a neutral molecule have been determined in the gas-phase. From this we determined the electric

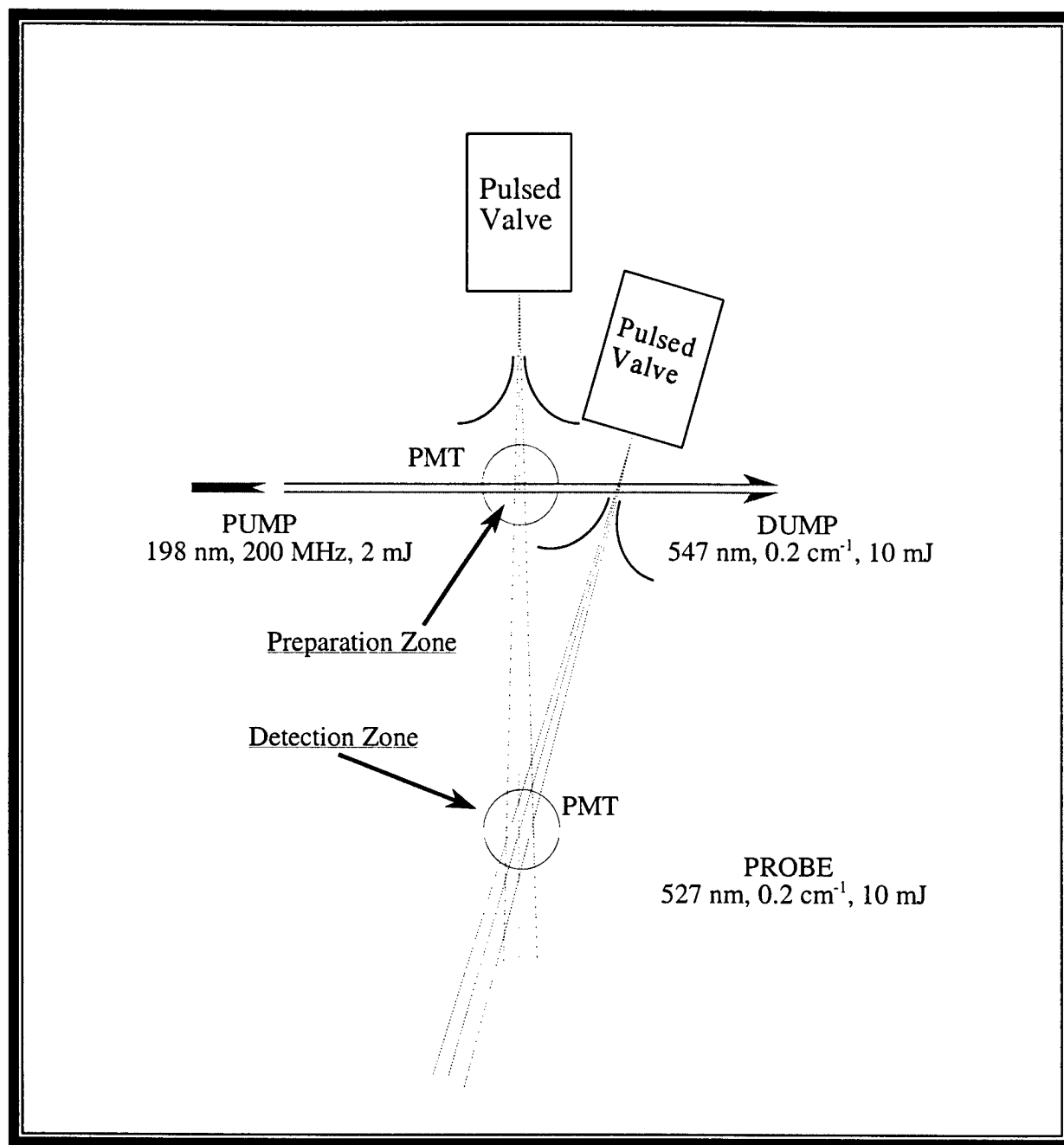


Figure 1 Schematic diagram of the crossed molecular beams machine. Two pulsed molecular beams are crossed in a single chamber. Stimulated emission pumping is used to prepare highly vibrationally excited NO in the primary (downward moving) beam using a pulsed dye amplifier laser system and an excimer pumped dye laser. Laser induced fluorescence is used at the crossing region of the two molecular beams to determine the state-to-state inelastic cross-sections using a second excimer pumped dye laser. The beam crossing region exists within the shadow of two skimmers and for several milliseconds after the pulsed beams are fired, a well defined crossed beam geometry is achieved. The experiment is repeated 10 times per second.

dipole moment function of the $\text{NO}(X^2\Pi)$ molecule, which we believe to be the definitive work. In addition to its practical value, the determination provides an excellent benchmark for *ab initio* theory.

We have also developed and optimized pulsed free-radical molecular beam sources that are suitable for use in similar multi-laser experiments. Due to this effort we now have a very strong NH free-radical beam source. In contrast to previous sources which also produced the first excited state $\text{NH}(a^1\Delta)$ using photolysis of NH_3 (4) or HNCO (5), this *pyrolysis* source provides exclusively ground state $\text{NH}(X^3\Sigma)$. The same *pyrolysis* source also produces strong pulsed beams of O -atoms and OH radicals using different precursor molecules.

Using the NH source, we investigated the radical-radical reaction $\text{NH} + \text{NO} \rightarrow \text{N}_2 + \text{OH}(v, N, \Omega)$ under single collision conditions in the "gas-phase machine". We observe the Doppler profile of the reactively scattered OH in individual quantum states (Fig. 2-- converted to velocity space). Absolute velocity calibration was achieved by simultaneously recording an I_2 calibration spectrum (not shown). One can see that the center of gravity of the Doppler profile is slightly shifted (by about 400 m/s) from zero velocity. This shift is due to the fact that the center-of-mass (CM) frame of the crossed beam collision system travels at constant velocity, \vec{V}_{CM} , with respect to the lab frame. The projection of this vector along the laser propagation direction is calculated (as observed) to be 400 m/s. See inset of Fig. 2. With this in mind one can see that the Doppler profile is symmetric about the projection of \vec{V}_{CM} , indicating forward-backward symmetry in the angular distribution. This provides an experimental reading of the lifetime of the collision complex, showing that the lifetime is greater than about 1 ps. This information determines the reactions mechanism (complex formation) and appears to settle a long-standing dispute between experiment (6) and theory (7) regarding this prototypical radical-radical reaction.

Using another apparatus in our laboratory (the "metastable machine"), we have recently examined the phenomenon of collisional alignment in seeded supersonic expansions (8-12). Simply by expanding a heavy (e.g. CO) molecule in a light carrier gas (e.g. He), molecular alignment is produced. This remarkable effect has been known for some time. Recently, however, velocity resolved experiments suggested that molecules of different

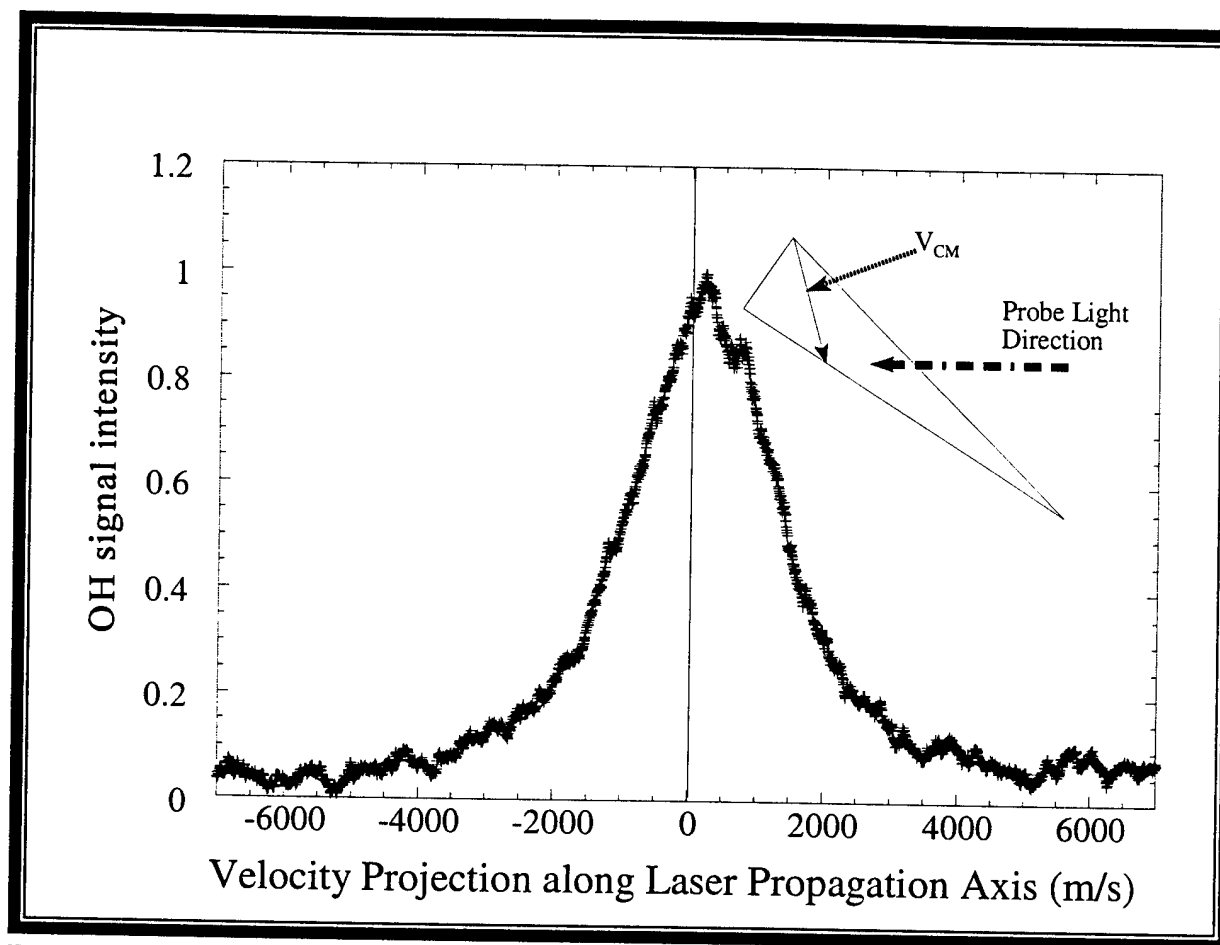


Figure 2 Doppler Profile of OH $P_1(1)$ ($1-0$) produced in the reaction $\text{NH} + \text{NO} \rightarrow \text{N}_2 + \text{OH}$, represented in velocity space. Absolute velocities were obtained from absolute wavelength calibrations against a simultaneously recorded I_2 spectrum (not shown). The Newton Diagram in the upper right hand corner shows that the laser propagation direction is nearly but not perfectly perpendicular to the velocity vector of the center-of-mass frame of reference. Therefore, the center of gravity of the Doppler profile is blue-shifted ~ 400 m/s from the velocity origin. The Doppler profile is symmetric about this velocity indicating forward-backward symmetry in the product angular distribution.

alignment could be separated by a velocity selector (9). We have performed quantum-state-specific neutral time-of-flight measurements (13) on molecular beams of dilute CO seeded in helium using polarized probe light, revealing the collisional alignment of individual rotational states of CO as a function of their terminal velocity. The derived peak velocities and translational temperatures depend on the probe-light polarization. CO molecules with their rotational angular momentum vectors, \vec{J} , aligned parallel to the flow velocity (propellers) are more effectively accelerated by the light carrier gas and reach a lower terminal translational temperature than molecules

with \vec{J} aligned perpendicular to the flow velocity (cartwheels). The results are qualitatively consistent with the idea that propellers have a larger total elastic cross section than cartwheels. Therefore, propellers suffer a larger average number of collisions in the expansion and are more effectively cooled.

Also using the metastable machine, long lived metastable states of acetylene have been detected. This work was carried out in Santa Barbara as part of a collaboration with Prof. R.W. Field of MIT. In this work we find UV excitation to metastable states of C_2H_2 above and below the dissociation limit. A strong S_1-T_3 interaction, located close in energy to the S_1 $3v_3$ (trans-bend) vibrational level is detected. A "gateway mediated intersystem crossing" singlet-triplet coupling mechanism explains the results. This is a new technique for spectroscopy of long lived triplet states and promises to give exciting results on the interactions of excited Singlet and Triplet states in polyatomic molecules. The initial exciting results obtained for Acetylene in Santa Barbara have stimulated Prof. Field to build a similar apparatus in Boston, so that this direction of research may be more rapidly pursued.

As mentioned above, we have also just finished construction and testing of a new surface science machine. A schematic diagram is shown in Fig. 3. It includes two triply differentially pumped molecular beam sources interfaced to an ultrahigh vacuum surface science chamber. The sources rely on high throughput booster pumps that can operate at as high as 10 mTorr total pressure ensuring maximum beam intensity. One molecular beam source is used to produce intense pulses of a molecule that can be pumped to a high vibrational state using stimulated emission pumping (SEP) (3). The second molecular beam source may be used to pre-dose the surface in order to create controlled surface over layers. The single crystal metal sample is mounted on a UHV feed-through manipulator. The UHV chamber is equipped with Argon Ion sputtering, AUGER and XPS for surface cleaning and characterization. In addition, a quadrupole mass spectrometer (not shown), equipped with a multi-channel scalar, is located in a differentially pumped UHV chamber and can be used to look for desorbing reaction products. A dual-MCP REMPI detection setup is also located in front of the surface in the UHV chamber to allow for state selective and mass-resolved laser based detection of scattered molecules.

This is a very ambitious project being carried out in collaboration with Dr. Daniel J. Auerbach of the IBM Almaden Research Center and the first results have only recently been obtained and await theoretical interpretation. Even so, these experiments show that the energy transfer characteristics of NO at oxidized Copper surfaces are markedly different when the NO contains large amounts of vibrational energy. Clear evidence of multiquantum vibrational relaxation was found as well as a strong dependence on the degree of oxidation of the Copper surface. While results are still very new, it is already clear that experiments such as these will aid in our still naive understanding of the interactions of highly vibrationally excited NO with surfaces.

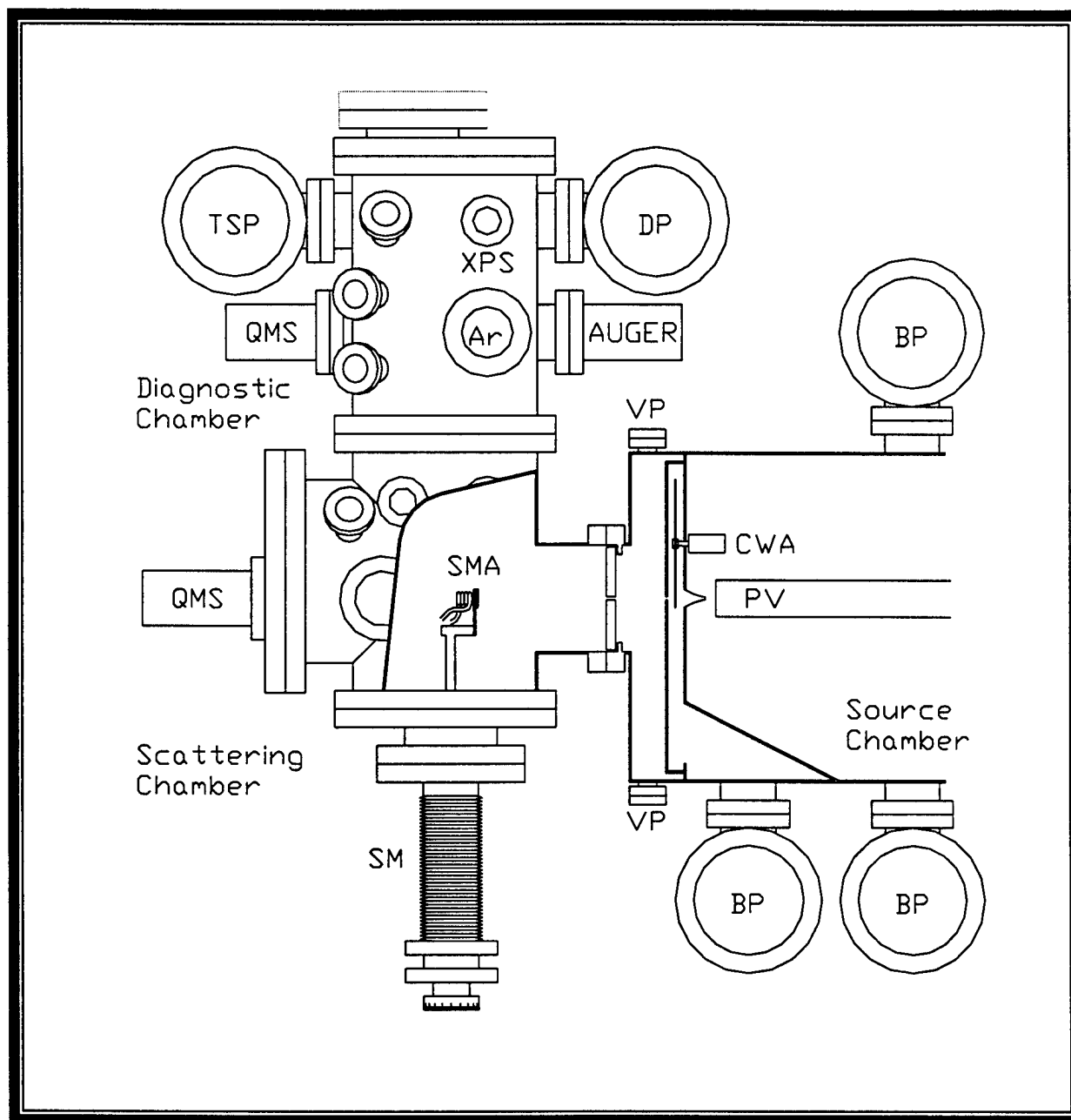


Figure 3 Schematic Diagram of the new surface scattering machine: Booster pumps (BP) evacuate the molecular beam source, within which a pulsed valve (PV) and a chopper wheel assembly (CWA) are housed. View Ports (VP) allow for access of the PUMP and DUMP laser beams. The Sample Manipulator (SM) controls the position and orientation of the Sample Assembly (SMA) within the UHV chamber, which is evacuated by a Diffusion pump (DP) and a Titanium Sublimation Pump (TSP). Three Quadrupole Mass Spectrometers (QMS) are available for: 1) beam diagnostics, 2) Temperature programmed desorption and 3) (not shown) surface scattering product detection. Argon Sputtering (Ar), Auger analysis (AUGER) and X-ray Photoelectron Spectroscopy (XPS) are used for surface preparation and analysis.

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4. *Anisotropic Translational Cooling: Velocity Dependence of Collisional Alignment in a Seeded Supersonic Expansion*, Steven Harich and Alec M. Wodtke, J. Chem. Phys. (Communication in press)
5. *Infrared and collisional relaxation of highly vibrationally excited NO: Applications of stimulated emission pumping in crossed and "uncrossed" molecular beams*, Marcel Drabbels and Alec M. Wodtke, in Highly Excited Molecules: Relaxation, Reaction and Structure, Eds. A.S. Mullin, G.C. Schatz, ACS Symposium Series, v. 678, p. 173 (1998)
6. *Rotational motion compensates the energy defect in near-resonant vibration-vibration energy transfer*, M. Drabbels, A.M. Wodtke J. Chem. Phys. *Rapid Communication* (In press)

Manuscripts in Preparation

1. *Pyrolysis source for intense pulsed molecular beams of O, OH, and NH*, H. Yuhui, A. M. Wodtke, Rev. Sci. Instr. (in progress)
2. *Forward-backward symmetry in the product angular distribution of $NH + NO \rightarrow OH + N_2$ by crossed-molecular beam Doppler velocimetry: Implications for the HNNO reaction-complex lifetime* H. Yuhui, A. M. Wodtke, (in progress)

Interactions/Transitions:

The infrared Einstein coefficient determinations yield the definitive Einstein coefficient matrix for use in modeling of infrared emission of atmospheric NO

Honors/Awards: Alexander von Humboldt Research Prize